

# **STUDY ON POLYCONDENSATION REACTIONS**

**A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of  
MASTER OF TECHNOLOGY**

00858

**by  
V. NANDA KUMAR**

**to the  
DEPARTMENT OF CHEMICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR  
AUGUST, 1982**

27 JUN 1988

CENTRAL LIBRARY  
111, Kinn

Acc. No. A 82800

CHE-1882 → M-KUM-STU

Thesis  
660-28!  
N153s

# CERTIFICATE

This is to certify that present work "Study on polycondensation reactions" has been carried out under my supervision and this has not been submitted elsewhere for a degree.

Date:

August 10, 1982

Dr. K.S. Gandhi  
Professor  
Department of Chemical  
Engineering,  
I.I.T. Kanpur 208016

## ACKNOWLEDGEMENT

I wish to express my sincere gratitude to Dr. K.S. Gandhi for his guidance and encouragement rendered to me all the time during my work. I would also like to extend my thanks to Mr. K.B.K. Rao and Mr. Alok Gupta for their useful discussions on several occasions.

I would like to thank Mr. M.M. Beg for his efficient typing and Mr. B.B. Srivastava for his excellent drawing.

To conclude my thanks to my friends Ezhil, Joshi and all others who helped me in one way or other.

V. NANDAKUMAR

CONTENTS

	Page
ACKNOWLEDGEMENT	(iii)
TABLE OF CONTENTS	(iv)
LIST OF FIGURES	(v)
LIST OF TABLES	(vi)
NOMENCLATURE	(vii)
ABSTRACT	(viii)
CHAPTER	
1 INTRODUCTION	1
2 KINETICS OF REVERSIBLE STEP POLYMERISATION	2
3 SIMULTANEOUS DIFFUSION AND POLYCONDENSATION	22
4 EXPERIMENTAL WORK	30
5 CONCLUSIONS	47
REFERENCES	48

## LIST OF FIGURES

Figures		Page
1	Effect of polycondensation reaction on the rate of mass transfer.	29
2	Sketch of the reactor.	32
3,4	GPC chromatograms for sample 1.	39
5,6	GPC chromatograms for sample 2.	41
7,8	GPC chromatograms for sample 3.	43

## LIST OF TABLES

Table		Page
1	Notations	4
2	Analysis of resin	37
3	Comparison between theoretical and experimental results	46

NOMENCLATURE

$k_1, k_2$	= forward reaction rate constants.
$k'_1, k'_2$	= reverse reaction rate constants
$t$	= time, sec.
$c_p, c_q,$ $c_z, c_v$	= concentrations of P, Q, Z and V respectively
$\bar{c}_p, \bar{c}_q$	= value of $c_p$ and $c_q$ in the main body of the liquid
$c_{vi}$	= value of $c_v$ at the phase boundary
$D$	= diffusivity, $\text{cm}^2/\text{sec}$ .
$\Delta t$	= time increment
$\Delta x$	= space increment
$M_G$	= molecular weight of propylene glycol
$M_A$	= molecular weight of adipic acid
$\bar{M}_n$	= number average molecular weight
$\bar{M}_w$	= weight average molecular weight
PDI	= poly dispersity index

## ABSTRACT

This work consists of two parts. In the first part, firstly the kinetics of reversible step polymerisation is discussed. The MWD for the reversible reaction involving asymmetric monomers is predicted to be same as that for irreversible reaction, if it is assumed that in a given species all the internal arrangements are equally probable. Secondly, an algorithm developed by Vimala and Nath was used to solve linear simultaneous partial differential equations describing mass transfer accompanied by polycondensation. In the second part an experimental apparatus that has been set up to perform polycondensation reactions has been described. The samples were analysed for acid number, hydroxyl number, water content. The samples were also analysed for molecular weight distribution by GPC. The  $\bar{M}_n$  calculated from acid and hydroxyl number is in good agreement with that calculated from theoretical considerations.

## CHAPTER 1

### INTRODUCTION

Several important polymers are produced by step polymerisation mechanism. In this type of polymerisation monomers with chemically reactive functional groups form the polymers. In the first part of this thesis, some theoretical work concerning reversible step polymerisation is presented. Firstly, molecular weight distribution in step polymerisation of two difunctional monomers one of them possessing structural asymmetry is calculated. Secondly a numerical technique for solving two simultaneous linear partial differential equations which arise out of simultaneous diffusion and polycondensation reaction is presented. In the second part of the thesis an experimental apparatus designed for carrying out polycondensation reactions is described and results of some experiments performed are presented.

## CHAPTER 2

### KINETICS OF REVERSIBLE STEP POLYMERISATION

Step polymers such as polyesters, polyurathanes, etc., can be considered as products of reaction between two difunctional monomers. Such polymerisations have been analysed using Flory's equal reactivity hypothesis. However examples of monomers for which the equal reactivity assumption is invalid are plenty. Three types of such monomers are

1. Asymmetric monomers in which the groups are not chemically equivalent, for example, a glycol with a primary and secondary hydroxyl groups whose reactivities are different

2. Cyclic monomers such as anhydrides. Here the anhydride group generates a carboxyl group on reaction with a hydroxyl group but the reactivities of carboxyl and anhydride groups are different.

3. Monomers with induced symmetry. In such monomers the functional groups are equally reactive till one of them reacts.

Case<sup>1</sup> presented the molecular weight distribution (MWD) in terms of the probabilities of reaction of functional groups. Gandhi and Babu<sup>2</sup> studied the effects of unequal

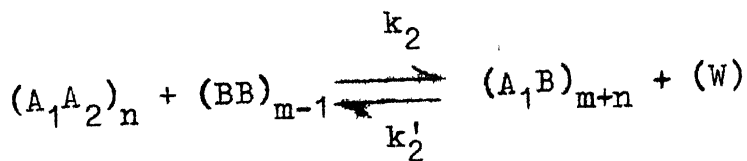
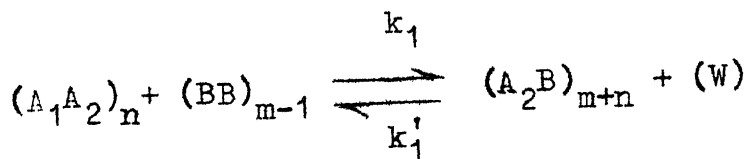
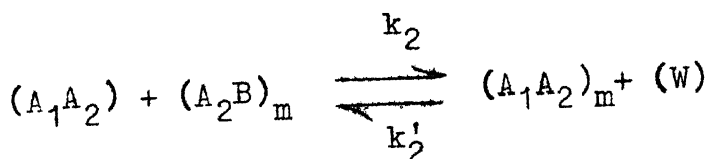
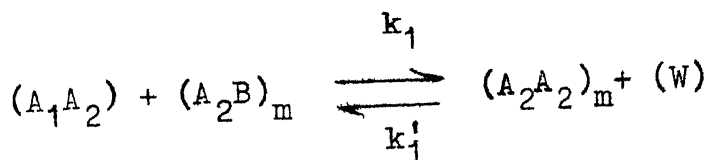
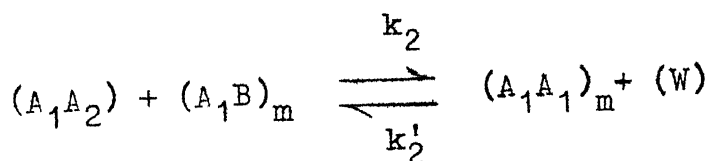
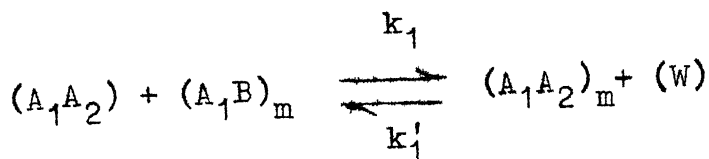
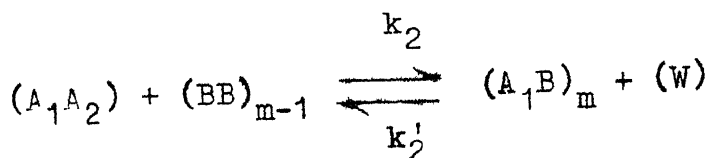
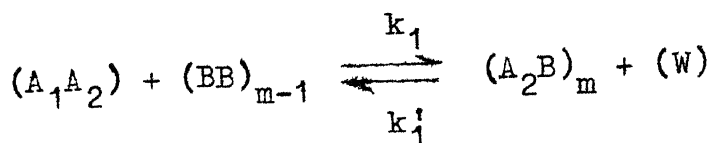
reactivity on the polymerisation kinetics and obtained these probabilities as functions of time for various values of the rate constants. In all of these studies, however, only irreversible reactions were studied. It is well known that Flory's distribution derived for irreversible equal reactivity case is also valid for reversible equal reactivity case. Numerical computations by Somu<sup>3</sup> for reaction mixtures initially containing stoichiometrically equal amounts of reactants indicate that the MWD for reversible as well as irreversible polymerisations at the same conversion are identical. In this work, it is intended to provide a theoretical understanding of the above result for reversible polymerisation reactions for asymmetric monomers.

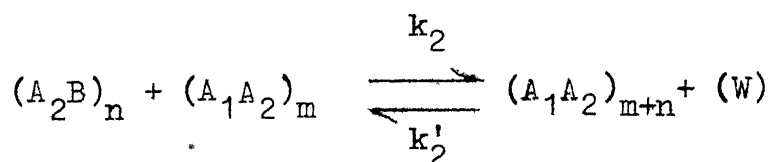
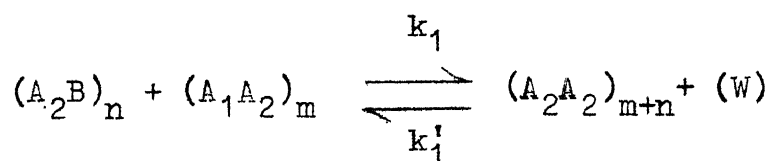
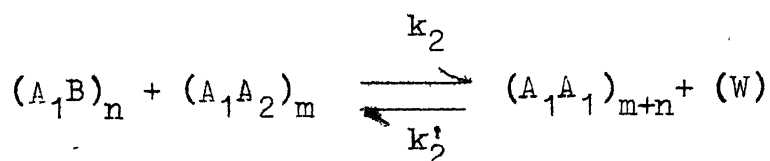
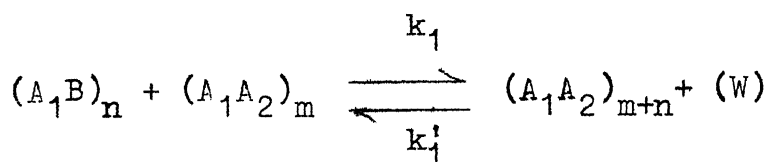
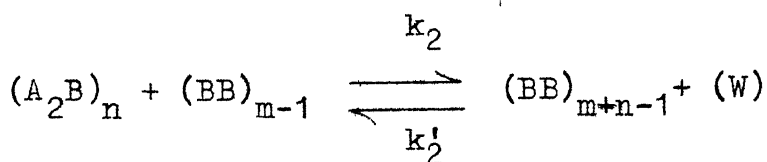
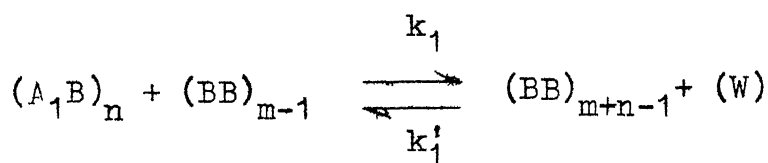
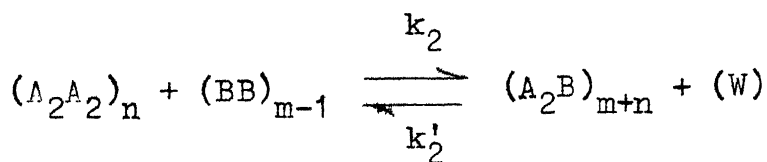
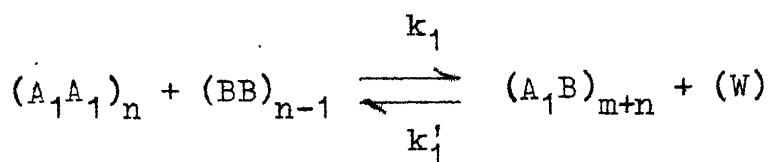
One common class of polymerisation which is often encountered is of the  $A_1A_2 + BB$  type, where  $A_1$ ,  $A_2$  and  $B$  are functional groups with  $A_1$  and  $A_2$  groups reacting with  $B$  groups at different rates. This is classified as asymmetry and it also implies that the reactivities of both the functional groups  $A_1$  and  $A_2$  are unaffected by the length of the chain at the end of which they are present. For such polymerisation involving asymmetric monomers, all the possible reactions that can occur between the functional groups will be listed first. The various types of molecules present at any time are given in Table 1.

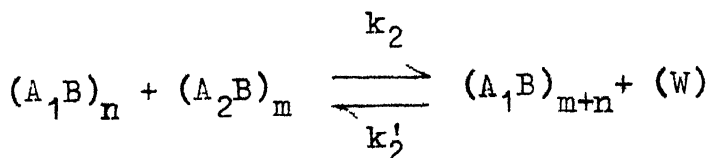
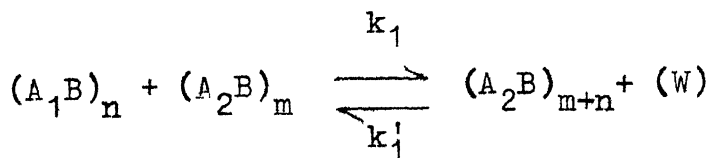
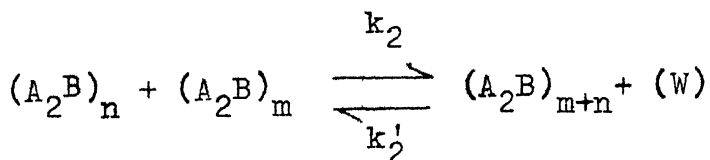
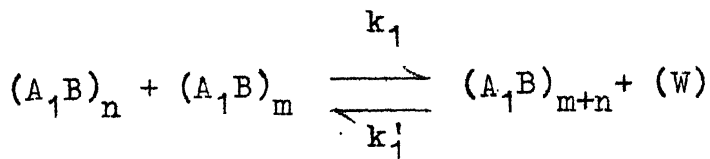
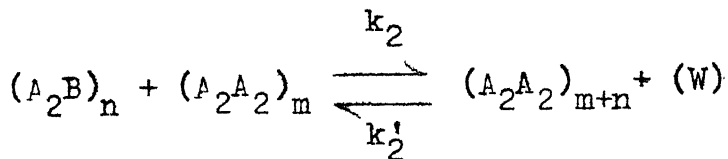
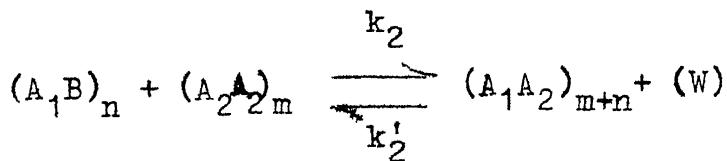
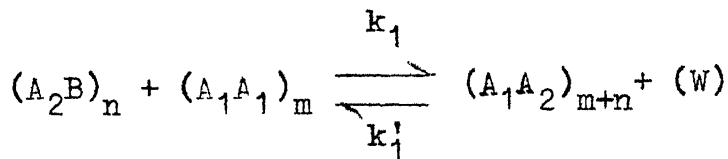
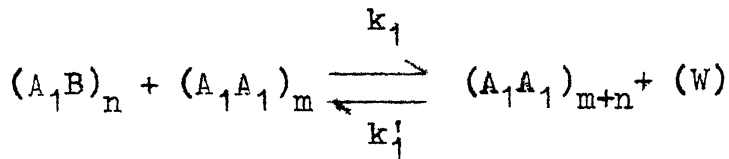
Table 1  
NOTATIONS

Type of species	Symbol used for representing species	Symbol used for representing concentration of species
$A_1A_2$	$(A_1A_2)$	$[A_1A_2]$
$(BBA_1A_2)_{n-1} BB$	$(BB)_{n-1}$	$[BB]_{n-1}$
$(A_1A_2BB)_n A_1A_2$	$(A_1A_2)_n$	$[A_1A_2]_n$
$(A_1A_2BB)_n A_2A_1$	$(A_1A_1)_n$	$[A_1A_1]_n$
$(A_2A_1BB)_n A_1A_2$	$(A_2A_2)_n$	$[A_2A_2]_n$
$(A_1A_2BB)_n$	$(A_1B)_n$	$[A_1B]_n$
$(A_2A_1BB)_n$	$(A_2B)_n$	$[A_2B]_n$
$W$	$(W)$	$[W]$

The reactions that can occur between the functional groups are as follows:







In the above equations W is being used to symbolize a side product that might be formed. It is to be emphasised

that the same rate constant for a given group is used irrespective of the chain length. The rate expressions for the disappearance of these species can be written as follows:

$$\begin{aligned}
 - \frac{d[A_1 A_2]}{dt} = & + 2k_1 [A_1 A_2] \sum_{n=1}^{\infty} [BB]_{n-1} \\
 & + 2k_2 [A_1 A_2] \sum_{n=1}^{\infty} [BB]_{n-1} \\
 & + k_1 [A_1 A_2] \sum_{n=1}^{\infty} [A_1 B]_n \\
 & + k_2 [A_1 A_2] \sum_{n=1}^{\infty} [A_1 B]_n \\
 & + k_1 [A_1 A_2] \sum_{n=1}^{\infty} [A_2 B]_n \\
 & + k_2 [A_1 A_2] \sum_{n=1}^{\infty} [A_2 B]_n \\
 & - k'_1 [W] \sum_{m=1}^{\infty} [A_2 B]_m \\
 & - k'_2 [W] \sum_{m=1}^{\infty} [A_1 B]_m \\
 & - k'_1 [W] \sum_{m=1}^{\infty} [A_1 A_2]_m \\
 & - 2k'_2 [W] \sum_{m=1}^{\infty} [A_1 A_1]_m \\
 & - 2k'_1 [W] \sum_{m=1}^{\infty} [A_2 A_2]_m \\
 & - k'_2 [W] \sum_{m=1}^{\infty} [A_1 A_2]_m
 \end{aligned} \tag{2.1}$$

$$\begin{aligned}
-\frac{d[BB]_{n-1}}{dt} = & + 2k_1 [BB]_{n-1} [A_1 A_2] \\
& + 2k_2 [BB]_{n-1} [A_1 A_2] \\
& + 2k_1 [BB]_{n-1} \sum_{m=1}^{\infty} [A_1 A_2]_m \\
& + 2k_2 [BB]_{n-1} \sum_{m=1}^{\infty} [A_1 A_2]_m \\
& + 4k_1 [BB]_{n-1} \sum_{m=1}^{\infty} [A_1 A_1]_m \\
& + 4k_2 [BB]_{n-1} \sum_{m=1}^{\infty} [A_2 A_2]_m \\
& + 2k_1 [BB]_{n-1} \sum_{m=1}^{\infty} [A_1 B]_m \\
& + 2k_2 [BB]_{n-1} \sum_{m=1}^{\infty} [A_2 B]_m \\
& + (k'_1 + k'_2) [W]_{(n-1)} [BB]_{n-1} \\
& - k'_1 [W] [A_2 B]_n \\
& - k'_2 [W] [A_1 B]_n \\
& - \frac{k'_1}{2} [W] \sum_{m=n+1}^{\infty} [A_2 B]_m
\end{aligned}$$

$$\begin{aligned}
& - \frac{k_2'}{2} [W] \sum_{m=n+1}^{\infty} [A_1 B]_m \\
& - \frac{k_1'}{2} [W] \sum_{m=n+1}^{\infty} [A_1 B]_m \\
& - \frac{k_2'}{2} [W] \sum_{m=n+1}^{\infty} [A_2 B]_m \\
& - k_2' [W] \sum_{m=n}^{\infty} [BB]_m \\
& - k_1' [W] \sum_{m=n}^{\infty} [BB]_m \\
& - 2k_1 \sum_{m=1}^{n-1} [BB]_{n-m} [A_1 B]_{m-1} \\
& - 2k_2 \sum_{m=1}^{n-1} [BB]_{n-m} [A_2 B]_{m-1}
\end{aligned} \tag{2.2}$$

$$\begin{aligned}
\frac{-d[A_1 A_2]_n}{dt} = & + 2k_1 [A_1 A_2]_n \sum_{m=1}^{\infty} [BB]_{m-1} \\
& + 2k_2 [A_1 A_2]_n \sum_{m=1}^{\infty} [BB]_{m-1} \\
& + k_1 [A_1 A_2]_n \sum_{m=1}^{\infty} [A_1 B]_m \\
& + k_2 [A_1 A_2]_n \sum_{m=1}^{\infty} [A_1 B]_m
\end{aligned}$$

$$\begin{aligned}
& + k_1 [A_1 A_2] \sum_{m=1}^{\infty} [A_2 B]_m \\
& + k_2 [A_1 A_2] \sum_{m=1}^{\infty} [A_2 B]_m \\
& + (k'_1 + k'_2) n [W] [A_1 A_2]_n \\
& - \frac{k'_1}{2} [W] \sum_{m=n+1}^{\infty} [A_2 B]_m \\
& - \frac{k'_2}{2} [W] \sum_{m=n+1}^{\infty} [A_1 B]_m \\
& - \frac{k'_1}{2} [W] \sum_{m=n+1}^{\infty} [A_1 A_2]_m \\
& - k'_2 [W] \sum_{m=n+1}^{\infty} [A_1 A_1]_m \\
& - k'_1 [W] \sum_{m=n+1}^{\infty} [A_2 A_2]_m \\
& - k'_2 [W] \sum_{m=n+1}^{\infty} [A_1 A_2]_m \\
& - k_1 [A_1 A_2] [A_1 B]_n \\
& - k_2 [A_1 A_2] [A_2 B]_n \\
& - k_1 \sum_{m=1}^{n-1} [A_1 A_2]_{n-m} [A_1 B]_m
\end{aligned}$$

$$\begin{aligned}
& - k_2 \sum_{m=1}^{n-1} [A_1 A_2]_{n-m} [A_2^B]_m \\
& - 2k_1 \sum_{m=1}^{n-1} [A_1 A_1]_{n-m} [A_2^B]_m \\
& - 2k_2 \sum_{m=1}^{n-1} [A_2 A_2]_{n-m} [A_1^B]_m
\end{aligned} \tag{2.3}$$

$$\begin{aligned}
\frac{-d [A_1 A_1]_n}{dt} = & + 2k_1 [A_1 A_1]_n \sum_{m=1}^{\infty} [A_1^B]_m \\
& + 2k_1 [A_1 A_1]_n \sum_{m=1}^{\infty} [A_2^B]_m \\
& + 4k_1 [A_1 A_1]_n \sum_{m=1}^{\infty} [BB]_{m-1} \\
& + k_2'(n+1) [W][A_1 A_1]_n \\
& + k_1'(n-1) [W][A_1 A_1]_n \\
& - \frac{k_1'}{2} [W] \sum_{m=n+1}^{\infty} [A_1^B]_m \\
& - \frac{k_1'}{2} [W] \sum_{m=n+1}^{\infty} [A_1 A_2]_m \\
& - k_1' [W] \sum_{m=n+1}^{\infty} [A_1 A_1]_m
\end{aligned}$$

$$\begin{aligned}
& - k_2 [A_1 A_2] [A_1 B]_n \\
& - k_2 \sum_{m=1}^{n-1} [A_1 A_2]_{n-m} [A_1 B]_m \\
& - 2k_1 \sum_{m=1}^{n-1} [A_1 A_1]_{n-m} [A_1 B]_m
\end{aligned} \tag{2.4}$$

$$\begin{aligned}
\frac{-d [A_2 A_2]_n}{dt} = & + 4k_2 [A_2 A_2]_n \sum_{m=1}^{\infty} [BB]_{m-1} \\
& + 2k_2 [A_2 A_2]_n \sum_{m=1}^{\infty} [A_2 B]_m \\
& + 2k_2 [A_2 A_2]_n \sum_{m=1}^{\infty} [A_1 B]_m \\
& + k'_1 (n+1) [W] [A_2 A_2]_n \\
& + k'_2 (n-1) [W] [A_2 A_2]_n \\
& - \frac{k'_2}{2} [W] \sum_{m=n+1}^{\infty} [A_2 B]_m \\
& - \frac{k'_2}{2} [W] \sum_{m=n+1}^{\infty} [A_1 A_2]_m \\
& - k'_2 [W] \sum_{m=n+1}^{\infty} [A_2 A_2]_m
\end{aligned}$$

$$\begin{aligned}
& - k_1 [A_1 A_2] [A_2 B]_n \\
& - 2k_2 \sum_{m=1}^{n-1} [A_2 A_2]_{n-m} [A_2 B]_m \\
& - k_1 \sum_{m=1}^{n-1} [A_1 A_2]_{n-m} [A_2 B]_m
\end{aligned} \tag{2.5}$$

$$\begin{aligned}
\frac{-d [A_1 B]_n}{dt} = & + k_1 [A_1 A_2] [A_1 B]_n \\
& + k_2 [A_1 A_2] [A_1 B]_n \\
& + 2k_1 [A_1 B]_n \sum_{m=1}^{\infty} [BB]_{m-1} \\
& + k_1 [A_1 B]_n \sum_{m=1}^{\infty} [A_1 A_2]_m \\
& + k_2 [A_1 B]_n \sum_{m=1}^{\infty} [A_1 A_2]_m \\
& + 2k_1 [A_1 B]_n \sum_{m=1}^{\infty} [A_1 A_1]_m \\
& + 2k_2 [A_1 B]_n \sum_{m=1}^{\infty} [A_2 A_2]_m \\
& + 2k_1 [A_1 B]_n \sum_{m=1}^{\infty} [A_1 B]_m \\
& + k_1 [A_1 B]_n \sum_{m=1}^{\infty} [A_2 B]_m
\end{aligned}$$

$$+ k_2 [A_1 B]_n \sum_{m=1}^{\infty} [A_2 B]_m$$

$$+ k_1' (n-1) [W][A_1 B]_n$$

$$+ k_2' n [W][A_1 B]_n$$

$$- k_1' [W][A_1 A_2]$$

$$- 2k_2' [W][A_1 A_1]_n$$

$$- k_1' [W] \sum_{m=n}^{\infty} [BB]_m$$

$$- \frac{k_1'}{2} [W] \sum_{m=n+1}^{\infty} [A_1 A_2]_m$$

$$- k_2' [W] \sum_{m=n+1}^{\infty} [A_1 A_1]_m$$

$$- k_1' [W] \sum_{m=n+1}^{\infty} [A_1 A_1]_m$$

$$- \frac{k_2'}{2} [W] \sum_{m=n+1}^{\infty} [A_1 A_2]_m$$

$$- k_1' [W] \sum_{m=n+1}^{\infty} [A_1 B]_m$$

$$- \frac{k_2'}{2} [W] \sum_{m=n+1}^{\infty} [A_2 B]_m$$

$$\begin{aligned}
& -k_2' [W] \sum_{m=n+1}^{\infty} [A_1 B]_m \\
& -k_2 [A_1 A_2] [BB]_{n-1} \\
& -2k_2 \sum_{m=1}^n [BB]_{n-m} [A_1 A_2]_{m-1} \\
& -4k_1 \sum_{m=1}^n [BB]_{n-m} [A_1 A_1]_{m-1} \\
& -2k_1 \sum_{m=1}^{n-1} [A_1 B]_{n-m} [A_1 B]_m \\
& -k_2 \sum_{m=1}^{\infty} [A_1 B]_{n-m} [A_2 B]_m
\end{aligned} \tag{2.6}$$

$$\begin{aligned}
\frac{-d[A_2 B]_n}{dt} = & +k_1 [A_1 A_2] [A_2 B]_n \\
& +k_2 [A_1 A_2] [A_2 B]_n \\
& +2k_2 [A_2 B]_n \sum_{m=1}^{\infty} [BB]_{m-1} \\
& +k_1 [A_2 B]_n \sum_{m=1}^{\infty} [A_1 A_2]_m \\
& +k_2 [A_2 B]_n \sum_{m=1}^{\infty} [A_1 A_2]_m \\
& +2k_1 [A_2 B]_n \sum_{m=1}^{\infty} [A_1 A_1]_m
\end{aligned}$$

$$\begin{aligned}
& + 2k_2 [A_2^B]_n \sum_{m=1}^{\infty} [A_2 A_2]_m \\
& + 2k_2 [A_2^B]_n \sum_{m=1}^{\infty} [A_2^B]_m \\
& + k_1 [A_2^B]_n \sum_{m=1}^{\infty} [A_1^B]_m \\
& + k_2 [A_2^B]_n \sum_{m=1}^{\infty} [A_1^B]_m \\
& + k'_1 n [W] [A_2^B]_n \\
& + k'_2 (n-1) [W] [A_2^B]_n \\
& - k'_2 [W] [A_1 A_2]_n \\
& - 2k'_1 [W] [A_2 A_2]_n \\
& - k'_2 [W] \sum_{m=n}^{\infty} [BB]_m \\
& - k'_1 [W] \sum_{m=n+1}^{\infty} [A_2 A_2]_m \\
& - \frac{k'_2}{2} [W] \sum_{m=n+1}^{\infty} [A_1 A_2]_m \\
& - \frac{k'_1}{2} [W] \sum_{m=n+1}^{\infty} [A_1 A_2]_m
\end{aligned}$$

$$\begin{aligned}
& - k_2' [W] \sum_{m=n+1}^{\infty} [A_2 A_2]_m \\
& - k_2' [W] \sum_{m=n+1}^{\infty} [A_2 B]_m \\
& - k_1' [W] \sum_{m=n+1}^{\infty} [A_2 B]_m \\
& - \frac{k_2'}{2} [W] \sum_{m=n+1}^{\infty} [A_1 B]_m \\
& - k_1 [A_1 A_2] [BB]_{n-1} \\
& - 2k_1 \sum_{m=1}^n [BB]_{n-m} [A_1 A_2]_{m-1} \\
& - 4k_2 \sum_{m=1}^n [BB]_{n-m} [A_2 A_2]_{m-1} \\
& - 2k_2 \sum_{m=1}^{n-1} [A_2 B]_{n-m} [A_2 B]_m \\
& - k_1 \sum_{m=1}^{n-1} [A_2 B]_{n-m} [A_1 B]_m
\end{aligned} \tag{2.7}$$

In deriving the above equations care has to be taken to account for chain breakage due to reverse reaction which can occur at two places and produce the same product. For example,  $(A_2 A_1)_n$  can produce  $A_1 A_2$  monomer by reverse reaction in two ways. In the above derivation one assumption was used. The symbol adopted for all the species do not

reflect all the internal arrangements. For example,  $(A_1B)_2$  actually consists of two types of molecules;  $A_1A_2BB$  and  $A_1A_2BB$  and  $A_1A_2BB$  and  $A_2A_1BB$ . It was assumed that both the species are equally probable in occurrence. This also implies that in a complicated molecule such as  $(A_2A_1)_n$  probabilities of occurrence of  $(A_1A_2BB)_m A_1A_2 (BBA_1A_2)_{n-m}$  and  $(A_1A_2BB)_m A_2A_1 (BBA_1A_2)_r$  are equal. Following the strong suggestion from Somu's<sup>3</sup> work, it is now intended to test whether the M.W.D. predicted for irreversible reactions is valid for the reversible reactions as well.

Let  $\alpha$ ,  $\beta$  and  $\gamma$  respectively represent the fraction of initial  $B, A_1$  and  $A_2$  groups that have reacted at any time. Then from stoichiometry

$$\alpha = \frac{R(\beta + \gamma)}{2} \quad (2.8)$$

where  $R = \frac{[A]_0}{[B]_0}$ . Here the initial group concentration

of both  $A_1$  and  $A_2$  is equal to  $[A]_0$ . Then Case's results on MWD for the irreversible polymerisation involving asymmetric monomer can be rearranged to give the following:

$$(BB)_{n-1} = B_0 (1-\alpha)^2 (R\beta\gamma)^{n-1}$$

$$(A_1B)_n = RB_0 (1-\beta) (1-\alpha)\gamma (R\beta\gamma)^{n-1}$$

$$(A_2B)_n = RB_0 (1-\alpha) (1-\gamma)\beta (R\beta\gamma)^{n-1}$$

$$\begin{aligned}
(A_1 A_1)_n &= R^2 B_0 (1-\beta)^2 \gamma^2 (R\beta\gamma)^{n-1} \\
(A_2 A_2)_n &= R^2 B_0 (1-\gamma)^2 \beta^2 (R\beta\gamma)^{n-1} \\
(A_1 A_2)_n &= R^2 B_0 (1-\beta)(1-\gamma)\beta\gamma (R\beta\gamma)^{n-1} \\
(A_1 A_2) &= R B_0 (1-\beta)(1-\gamma) \quad (2.9)
\end{aligned}$$

If the unreacted  $A_1$  group concentration is  $[A_1]$ , the initial  $A_1$  group concentration is  $[A]_0$  and the unreacted B group concentration is  $[B]$  then intuitively one would expect the over all rate equation for  $[A_1]$  to be

$$-\frac{d[A_1]}{dt} = k_1[A_1][B] - k_1'[W][A]_0 - [A_1]$$

similar equations might also be expected for unreacted  $A_2$  and B group concentrations. As a justification for the assumption made in deriving equations (2.1) to (2.7), it can be said that the above intuitive expressions can be obtained from equations (2.1) to (2.7) by observing that

$$[A_1] = [A_1 A_2] + \sum_{n=1}^{\infty} 2[A_1 A_1]_n + \sum_{n=1}^{\infty} [A_1 B]_n + \sum_{n=1}^{\infty} [A_1 A_2]_n$$

and summing the appropriate rate equations. As a consequence,

the relationship between  $\beta$  and  $\gamma$  given by Gandhi and Babu<sup>2</sup>

$$(1-\beta)^{k_2} = (1-\gamma)^{k_1} \quad (2.10)$$

is also valid.

If (2.9) is a solution to equations (2.1) to (2.7), then substitution of (2.9) into the LHS and RHS of any one of equations (2.1) to (2.7) must all yield the same equation. If equation (2.9) is substituted in equation (2.1) with the help of equations (2.8) and (2.10), equation (2.1) after subsequent mathematical simplification is reduced to give

$$\frac{d\beta}{dt} = 2 k_1 B_0 (1-\alpha)(1-\beta) - k_1 [W]\beta$$

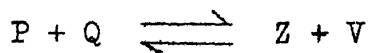
Further when equation (2.9) is substituted in any of the rate expressions (2.2) to (2.7) and after use of equation (2.8) and (2.10) the same result is obtained. So the MWD predicted for asymmetric monomers in the case of irreversible reaction is also valid for reversible case.

Thus it can be concluded that if one assumes that in a given species all internal arrangements are equally probable, the MWD for reversible as well as irreversible step polymerisations with unequal reactivities are identical at a given conversion.

### CHAPTER 3

#### SIMULTANEOUS DIFFUSION AND POLYCONDENSATION

For several polycondensation processes the rate of conversion is not only determined by the chemical reaction rate, but also by the rate of removal of the volatile byproduct. Combination of mass transfer and chemical reaction have been studied in the case of gas absorption. The same methods may be used for polycondensation reactions. In the initial stages, the volatile product is easily removed. As the degree of polymerisation increases, the desorption rate is more important. Finally when chemical equilibrium is reached, the rate of conversion becomes equal to the shift of equilibrium composition with time and largely depends on the rate of mass transfer. It is for this later stage of polycondensation process that theoretical equations are obtained for the rate of interphase mass transfer accompanied by chemical reaction. The reaction for a polycondensation process can be written as

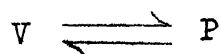


in which P and Q are reacting end groups, Z is the resulting ester group and V is the volatile component produced. For unsteady diffusion accompanied by reaction or for application

of penetration model, the following differential equation is valid for the concentration of volatile component.

$$\frac{\partial C_V}{\partial t} = D \frac{\partial^2 C_V}{\partial x^2} + k_c \left( C_p C_q - \frac{C_V C_Z}{K_C} \right) \quad (3.1)$$

where  $k_c$  is the condensation rate constant and  $K_C$  is the equilibrium constant. The above nonlinear equation can be transformed into a first order system. The linearisation is made by assuming that deviations from mean concentration are small due to short contact times compared with the time necessary to produce a significant difference in the mean values of the concentrations of non-volatile component. So the deviation from equilibrium is small. Such a procedure has been suggested by Van Krevelen<sup>4</sup>. Following his work, the polycondensation reaction is now written as quasi first-order reaction.



The concentrations  $C_A$  and  $C_B$  are defined as the distance from the equilibrium for V and P. The transformation is thus performed by introducing

$$C_A = C_V - \frac{\bar{C}_p \bar{C}_q K_c}{\bar{C}_z}$$

$$C_B = C_p - \bar{C}_p \quad (3.2)$$

and

$$k = \frac{k_c \bar{C}_z}{K_c} ; \quad K = \frac{\bar{C}_z}{\bar{C}_p K_c}$$

in which  $C_V$  and  $C_P$  are the local concentrations of V and P and  $\bar{C}_p$ ,  $\bar{C}_q$  and  $\bar{C}_z$  are mean concentrations in the bulk of the liquid.

With the help of equation (3.2), equation (3.1) can be transformed to

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial x^2} - k (C_A - C_B/K) \quad (3.3)$$

In the same way, one can write

$$\frac{\partial C_B}{\partial t} = D \frac{\partial^2 C_B}{\partial x^2} + k (C_A - C_B/K) \quad (3.4)$$

$$\text{Initial conditions: at } t=0, C_A = 0; C_B = 0 \quad (3.5)$$

$$\text{Boundary conditions: at } t > 0, x = 0, C_A = C_{A0} (C_V = C_{Vi})$$

$$\frac{\partial C_B}{\partial x} = 0 \quad (3.6)$$

$$\text{at } t > 0, x = \infty, C_A = 0, C_B = 0 \quad (3.7)$$

The initial condition is a state of equilibrium throughout the liquid. Desorption of component V starts at  $t=0$ .

The B.C.(3.6) defines a quantity  $C_{Vi}$  being the value of  $C_V$  at the phase boundary in equilibrium with the vapour phase and also means that P can not desorb. The B.C. (3.7) means that far away from the phase boundary chemical equilibrium

exists. The instantaneous supply rate per unit surface area,  $N_A$ , is given by

$$t_1 N_A = \int_0^{\infty} C_A dx + \int_0^{\infty} C_B dx$$

Mathematical computation:

A numerical solution of equations (3.3) and (3.4) subject to I.C.(3.5) and B.C.(3.6) and (3.7) is obtained by converting them into a set of implicit finite difference equations and solving the tridiagonal matrix equation on a computer by making use of a suitable algorithm.

Equations (3.3) and (3.4) are non-dimensionalised by using the following variables.

$$a = \frac{C_A}{C_{A0}} ; b = \frac{C_B}{C_{B0}} ; T = kt ; X = x \sqrt{\frac{k}{D}}$$

to give

$$\frac{\partial a}{\partial t} = \frac{\partial^2 a}{\partial X^2} - (a - b/K)$$

(3.8)

$$\frac{\partial b}{\partial t} = \frac{\partial^2 b}{\partial X^2} + (a - b/K)$$

Now the I.C. : at  $T = 0$ ,  $a = 0$  ;  $b = 0$

B.C. → at  $T > 0$ ,  $X = 0$ ,  $a = 1$ ;  $\frac{\partial b}{\partial X} = 0$

at  $T > 0$ ,  $X = \infty$ ,  $a = 0$ ;  $b = 0$

When equation (3.8) is written in forward finite difference, it leads to

$$\frac{a_{n,m+1} - a_{n,m}}{\Delta T} = \frac{a_{n-1,m+1} - 2a_{n,m+1} + a_{n+1,m+1}}{\Delta X^2} - (a_{n,m+1} - b_{n,m+1})/K$$

$$\frac{b_{n,m+1} - b_{n,m}}{\Delta T} = \frac{b_{n-1,m+1} - 2b_{n,m+1} + b_{n+1,m+1}}{\Delta X^2} + (a_{n,m+1} - b_{n,m+1})/K$$

which in turn written in matrix form gives

$$\begin{bmatrix} -\frac{1}{\Delta X^2} & 0 \\ c & -\frac{1}{\Delta X^2} \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix}_{n-1,m+1} + \begin{bmatrix} \frac{1}{\Delta T} + \frac{2}{\Delta X^2} + 1 & -\frac{1}{K} \\ -1 & \frac{1}{\Delta T} + \frac{2}{\Delta X^2} + \frac{1}{K} \end{bmatrix}$$

$$\begin{bmatrix} a \\ b \end{bmatrix}_{n,m+1} + \begin{bmatrix} -\frac{1}{\Delta X^2} & 0 \\ c & -\frac{1}{\Delta X^2} \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix}_{n+1,m+1} = \begin{bmatrix} \frac{a}{\Delta T} \\ \frac{b}{\Delta T} \end{bmatrix}_{n,m}$$

This can be rewritten in a convenient form

$$A_n W_{n-1} + B_n W_n + C_n W_{n+1} = D_n \quad (3.9)$$

It may be noted that  $D_n$  is at a time level  $m$  where as all  $W$ 's are at an advanced time level  $m+1$ . The matrices  $A_n$ ,  $B_n$  and  $C_n$  are constant and known. An algorithm given by Vimala and Nath<sup>5</sup> can be used to obtain the solution  $W_n$  at  $m+1$  :

$$W_n = -E_n W_{n+1} + J_n \quad 1 \leq n \leq N-1 \quad (3.10)$$

where

$$\left. \begin{aligned} E_n &= (B_n - A_n E_{n-1})^{-1} C_n \\ J_n &= (B_n - A_n E_{n-1})^{-1} (D_n - A_n J_{n-1}) \end{aligned} \right\} 2 \leq n \leq N-1 \quad (3.11)$$

$$\text{Using B.C; } E_1 = - \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}; E_N = \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix}$$

$$J_1 = \begin{bmatrix} 1 \\ 0 \end{bmatrix}; J_N = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \quad (3.12)$$

By equations (3.10) and (3.12)

$$W_N = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$\text{and by I.C } W_1 = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

Knowing the values of dependent variables at  $m$ , i.e. corresponding to  $T$ , the dependent variable  $W_n$  at  $m+1$ , i.e. at  $T + \Delta T$  can be computed by adopting the following procedure.

First, the values of matrix elements  $A_{11}$ ,  $B_{11}$ ...etc. are evaluated. Next with the help of equations (3.11) and (3.12)  $E_n$  and  $J_n$  based on the value of the variables at  $m$  are calculated for all  $n$  between 1 and  $N$ , starting from  $n = 1$  and proceeding to  $n = N$ . By substituting the values of  $E_n$  and  $J_n$  in (3.10) and using B.C.(3.12), the values of the dependent variables  $W_n$  at  $m+1$  are then determined in the reverse order i.e. starting from  $n = N$ . The so obtained values of  $W_n$  at  $m+1$  can then be used to obtain  $W_n$  at  $m+2$  and so on. The mass transfer rate was evaluated in terms of dimensionless groups appearing in the proposed equation

$$\frac{\bar{N}_A}{[A_0]V D k} = \frac{1}{T_1} \left[ \int_0^\infty a \, dx + \int_0^\infty b \, dx \right]$$

The mass transfer rate is evaluated for various values of equilibrium constant. This has been plotted against  $T$ , with the equilibrium constant  $K$  as parameter in figure 1. Sherwood and Pigford<sup>6</sup> presented an analytical solution for the problem. It can be observed that the algorithm given by Vimla and Nath<sup>5</sup> is satisfactory. It was intended to apply this algorithm to convective mass transfer but could not be completed.

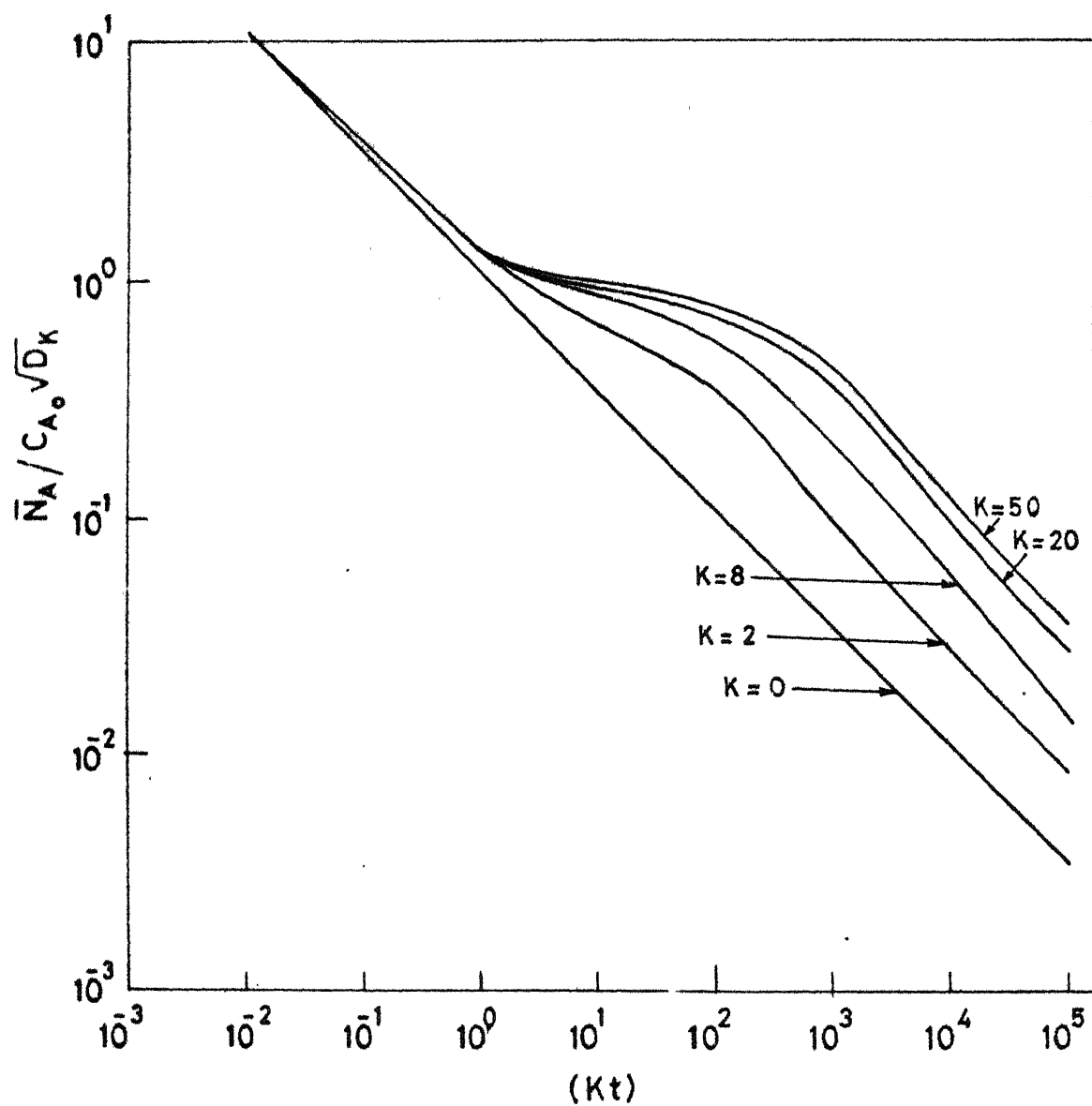


Fig.1. Effect of polycondensation on the rate of mass transfer

## CHAPTER 4

### EXPERIMENTAL WORK

Polycondensation is a process of obtaining high molecular weight compounds. This process is generally accompanied by the simultaneous elimination of some low molecular weight by product. Polycondensations are reversible and can reach an equilibrium. The establishment of the equilibrium is determined by the conditions of the condensation. In order to obtain polyesters with a high molecular weight it is necessary to select conditions ensuring the displacement of the equilibrium in the direction of the formation of the polyester molecule. This can be achieved only with the maximum elimination of low molecular weight by products from the reaction. So polycondensation is generally performed in two stages. First the reaction mixture is heated in a current of nitrogen gas to ensure an inert atmosphere which prevents the degradation of higher molecular weight components and facilitates the elimination of low molecular weight reaction products from the reaction medium. In the second stage heating is continued in vacuum to eliminate the low molecular weight by products more completely. It was the aim of the experimental work to setup an apparatus where polycondensation reactions could be studied experimentally.

### Apparatus:

A cylindrical glass reactor of two litre capacity with a flange was used for carrying out the condensation polymerisation. In order to cover the reactor, a S.S. plate of diameter slightly bigger than that of the reactor was made. Threads were cut at the centre so that a bush could be fixed. In the bush a hole of diameter almost equal to that of stirrer rod was made. A bearing was inserted on the top of the bush in order to allow free rotation of the stirrer. The sketch of the reactor is shown in Figure 2. Care was taken to avoid leaks by fixing the bearing tightly. Three more holes were made on the plate for inlet gas (Nitrogen) tube, condenser and thermometer respectively. The inlet gas tube was extended upto bottom of the reactor so that the nitrogen can bubble through the mixture. Only 50 mm Hg vacuum could be reached in this apparatus.

### Starting materials:

Adipic acid and propylene glycol were used as starting materials. 99% pure adipic acid (SDS make) having a melting point of 150°C and propylene glycol (analaar grade, pfizer reagent) were used. Adipic acid and propylene glycol were taken as starting materials so that water analysis could be made which requires that unsaturation bonds be not present and so that liquid (noncrystalline) resins could be produced.

Rec. No. A... 32800

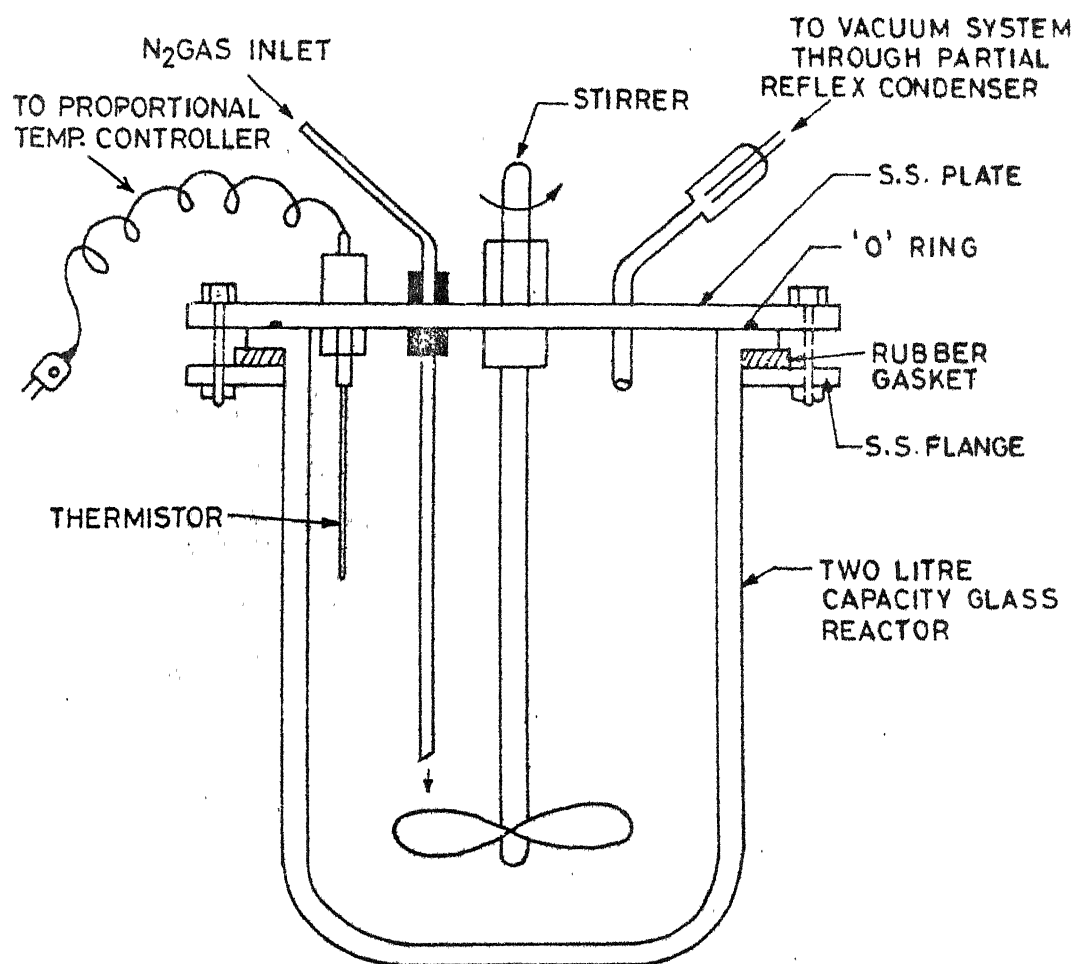


FIG.2 SKETCH OF THE REACTOR

Procedure:

For the synthesis of polypropylene glycol adipate, adipic acid and propylene glycol were used as the starting materials. The starting materials were placed in a two litre capacity cylindrical glass reactor. The reaction mixture was heated by a heating mantle and the temperature was controlled by a proportional controller. Adipic acid and propylene glycol were taken in equimolar ratio. Propylene glycol was taken 5% in excess to prevent the loss of more volatile component from the reaction medium during the reaction. The reactants were preheated before they were placed together in the reactor. p-toluene sulfonic acid (0.015 equivalent/kg of reaction mixture) was added as a catalyst. The reaction mixture was heated with continuous passage of a current of nitrogen. The heating was carried out for six hours at 180°C. A sample was taken out for analysis. Then, further heating was carried out at 150°C in a vacuum of 50 mm Hg for three more hours. A second sample was withdrawn from the reactor at the end of ninth hour. The temperature was again increased to nearly 190°C and the reaction was carried out for three more hours in a vacuum of 50 mm Hg. A third sample was taken out at the end of the reaction. The samples were analysed for acid number, hydroxyl number,

number average molecular weight from the end group analysis and the water content in the sample. The samples were also analysed in GPC (Gel permeation chromatography, waters Association, U.S.A.) for molecular weight distribution.

Analytical procedure:

Determination of acid number: The acid number is defined as the number of mgs of KOH required to neutralize the carboxyl group in 1 gm. of acid. For the determination of acid number, a weighed sample of the resin was dissolved in a mixture of methanol, benzene and isopropanol and titrated against an alcoholic solution of KOH in the presence of phenolphthalein as indicator.

$$\text{Acid number} = \frac{a \times k \times 56.1}{b}$$

where

a = ml of KOH used in the titration.

k = normality of KOH

b = weight of the sample in gms.

Determination of hydroxyl number: The hydroxyl number is expressed in milligrams of KOH required to neutralise the acetic acid entering into the composition of acetylated product obtained from 1 gm. of substance under investigation.

An Acetylation mixture was prepared by mixing 120 ml of acetic anhydride and 880 ml of anhydrous pyridine. A blank experiment was first carried out. For this, 10 ml of the acetylating mixture was titrated against a KOH solution in the presence of phenolphthalein. The acetylating mixture (20 ml) was added to the sample and was heated on a water bath for 15 minutes. After cooling, 25 ml of water was added, the mixture was cooled, and then titrated against KOH.

$$\text{Hydroxyl number} = \frac{(a+b-c) \times k \times 56.1}{d}$$

where

- a = ml of KCH that were used to neutralise the acid
- b = ml of KOH consumed in blank experiment
- c = ml of KOH consumed in the working experiment
- d = weight of the sample

Determination of water: Water was analysed by Karl-Fischer titration.

The conditions used for GPC analysis were as follows:

Columns employed :  $10^4 \text{ \AA}$ ,  $10^3 \text{ \AA}$ ,  $500 \text{ \AA}$

Solvent : Chloroform

Elution rate: 1 ml/min

Calibration was done with Dodecyl mercaptan, and 2900, 4000, 9000, 50000 polystyrene standard.

Detector: Refractive index (401 Model), sensitivity 4X.

## Results and Discussion:

The analytical results of the resin are presented in Table 2. As the experiment proceeds, inspite of the partial condenser some ethylene glycol does vaporise. So the initial ratio of Glycol to Adipic acid will not be the proper ratio to use at all times. To avoid this difficulty, monitoring of the ethylene glycol in the condensate is to be done. In this work, to perform theoretical calculations it will be assumed that equilibrium has been **achieved**. This is justified by the following calculations:

$$\begin{aligned} \text{Equilibrium constant} &\propto \frac{(\text{Acid number})(\text{Hydroxyl number})}{(\text{water})(\text{ester group})} \\ &\propto \frac{(\text{Acid number})(\text{Hydroxyl number})}{(\text{water})(\text{Number average molecular weight})} \end{aligned}$$

Further the number average molecular weight is given by half of sum of end groups or is proportional to half of sum of Acid number and Hydroxyl number.

$$\text{Equilibrium constant} \propto \frac{(\text{Acid number})(\text{Hydroxyl number})}{(\text{Water})(\text{Acid number} + \text{Hydroxyl number})}$$

These numbers for all the three resins are approximately the same. Hence it is reasonable to assume equilibrium has been reached. In theoretical calculations it was therefore assumed

Table 2ANALYSIS OF RESINS

Resin number	Acid number	Hydroxyl number	Water content wt. %	(Acid number+ Hydroxyl number)/2
1	77.5	60.2	1.20	68.8
2	41.3	40.5	0.62	40.9
3	23.8	20.8	0.36	22.3

that each resin was obtained from a resin whose initial glycol to acid ratio would be that which is consistent with the observations. Thus if  $\beta$  is the conversion of hydroxyl groups, and if R moles of glycol were taken per mole of acid, then

$$\frac{\text{Acid number} \times 10^{-3}}{56.1} = \frac{2(1-R\beta)}{RM_G + M_A - 18R\beta}$$

$$\frac{\text{Hydroxyl number} \times 10^{-3}}{56.1} = \frac{2R(1-\beta)}{RM_G + M_A - 18R\beta}$$

From this R and  $\beta$  could be calculated. From results of Gandhi and Babu<sup>2</sup>

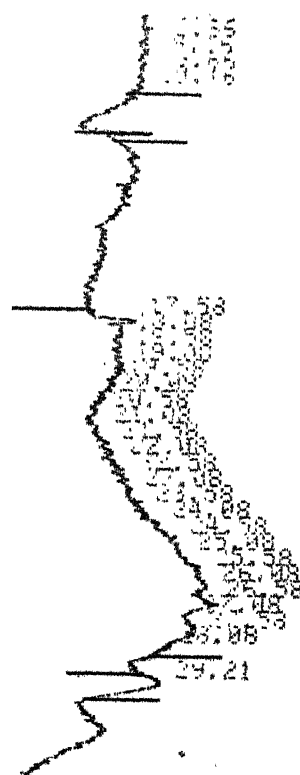
$$\bar{M}_n = (RM_G + M_A) / (R + 1 - 2\alpha)$$

$$PDI = (R + 1 - 2\alpha)$$

$$\frac{M_A^2(1 + R\beta^2) + 4\alpha M_G M_A + M_G^2(R + R^2\beta^2)}{(1 - R\beta^2)(RM_G + M_A)^2}$$

The calculated values of R and  $\beta$  were then used to compute  $\bar{M}_n$  and PDI for each resin. These are given in Table 3.

GPC results are presented in figures 3 to 9. Duplicate runs are also presented for comparison. Firstly the molecular weight can only be in increments of  $(M_G + M_A - 18)$  or approximately 200. While this does not pose any problem for high molecular weight samples, at low molecular weights it causes errors as



AUG. 6, 1992 16:37:22

CHHPT 0.50 CM-MIN

RUN #5

CHLC #1

COLUMNS:  $10^4 \text{Å}$ ,  $10^3 \text{Å}$ ,  $500 \text{Å}$ 

SOLVENT: CHLOROFORM

OPP ID

GPC QUANTITATION

CHROMATOGRAM OF SAMPLE 1

RT	AREA	MOL WT	REF MW	
24.58	2789500	0.149181E4	0.186987E4	F
24.58	7480040	0.114510E4	0.651474E4	F
25.08	10811800	0.875372E3	0.123510E5	F
25.52	14608400	0.665786E3	0.319415E5	F
26.48	17241600	0.503500E3	1.342434E5	F
26.58	17104100	0.378100E3	1.452099E5	F
27.08	15402400	0.260350E3	1.545443E5	F
27.58	13236400	0.202900E3	1.533087E5	F
28.08	8406130	0.153500E3	1.147523E5	F
29.45	1055780	0.121400E3	1.369162E4	L

NO-AUG 0.356310E3

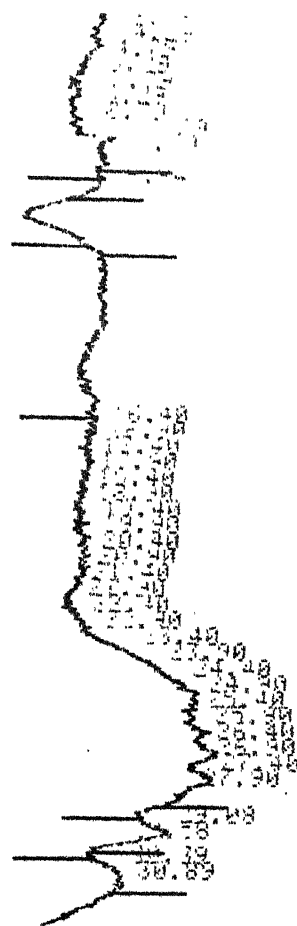
WT-AUG 0.514092E3

Z-AUG 0.712280E3

VIS-AUG 0.513963E3

DISPERSITY 0.144282E1

INTRINSIC VISCOSITY 0.513932E-3



AUG. 6, 1982 17:17:54

CHART 0.50 CM/MIN

COLUMNS: 10<sup>4</sup>Å, 10<sup>3</sup>Å, 500Å

RUN #6

SOLVENT: CHLOROFORM

LALC #1

OPR 10

3

GPC QUANTITATION

CHROMATOGRAM OF SAMPLE 1 (REPEAT)

RT	AREA	MOL WT	W <sub>g</sub> MW	
23.90	1969820	0.163948E4	0.120149E4	F
24.40	8599450	0.126030E4	0.682333E4	F
24.90	14814600	0.964931E3	0.153530E5	F
25.40	15102600	0.735077E3	0.205456E5	F
25.90	14222300	0.557163E3	0.255262E5	F
26.40	15881600	0.419778E3	0.378333E5	F
26.90	17535200	0.314030E3	0.558392E5	F
27.40	13175200	0.233235E3	0.564932E5	F
27.90	12913200	0.171816E3	0.751571E5	F
28.38	4762990	0.127028E3	0.374955E5	L

NO-AVG 0.358076E3

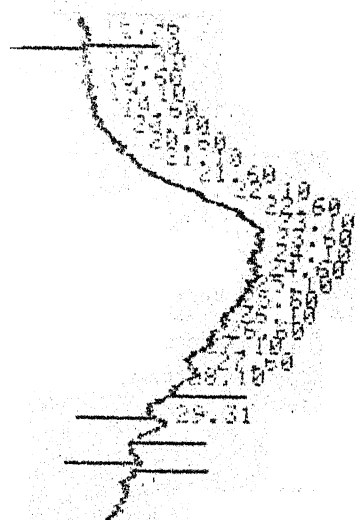
WT-AVG 0.550177E3

Z-AVG 0.779513E3

VIS-AVG 0.550070E3

DISPERSITY 0.153648E1

INTRINSIC VISCOSITY 0.549960E-3



AUG. 6, 1982 15:19:51

CHART 0.50 CM/MIN

RUN #3

CALC #1

COLUMN:  $10^4 \text{Å}$ ,  $10^3 \text{Å}$ ,  $500 \text{Å}$ 

SOLVENT: CHLOROFORM

OFF ID:

5

GPC QUANTITATION

CHROMATOGRAM OF SAMPLE 2

RT	AREA	MOL WT	A-MW	
20.10	125610	0.114217E5	0.109974E2	F
20.80	3456470	0.884829E4	0.390637E3	F
21.10	7236750	0.486275E4	0.105449E4	F
21.60	14006100	0.532613E4	0.262969E4	F
22.10	23847400	0.413358E4	0.576918E4	F
22.60	73115500	0.320472E4	0.103333E5	F
23.10	78113500	0.248096E4	0.153624E5	F
23.60	37647400	0.191670E4	0.196417E5	F
24.10	35819300	0.147630E4	0.237209E5	F
24.60	33957700	0.113291E4	0.299738E5	F
25.10	30612700	0.865839E3	0.353561E5	F
25.60	26050500	0.658403E3	0.395661E5	F
26.10	21558100	0.497771E3	0.433092E5	F
26.60	16953300	0.374017E3	0.453289E5	F
27.10	11424700	0.279060E3	0.409399E5	F
27.60	6675560	0.206583E3	0.419955E5	F
28.10	4593840	0.151632E3	0.302959E5	F
29.42	306060	0.123839E3	0.247149E4	L

NO-AUG 0.893216E3

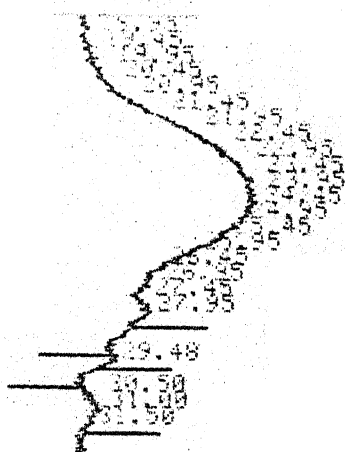
M1-AUG 0.157377E4

M2-AUG 0.337396E4

M3-AUG 0.197335E4

DISPERSITY 0.220973E1

INTRINSIC VISCOSITY 0.197295E-2



AUG. 6. 1982 15:58:16

CHART 0.50 CM/MIN

COLUMNS:  $10^4 \text{Å}$ ,  $10^3 \text{Å}$ ,  $500 \text{Å}$ 

RUN #4

SOLVENT: CHLOROFORM

ALC #1

UPR 10

5

## GPC QUANTITATION

## CHROMATOGRAM OF SAMPLE 2 (REPEAT)

RT	AREA	MOL WT	M/NM	
20.45	158395	0.954897E4	0.165876E2	F
20.95	4873780	0.740545E4	0.550105E3	F
21.45	10719900	0.574790E4	0.186501E4	F
21.95	19950800	0.446005E4	0.447322E4	F
22.45	28000400	0.345954E4	0.809367E4	F
22.95	34116800	0.267959E4	0.127320E5	F
23.45	38111700	0.207152E4	0.183979E5	F
23.95	40196000	0.159719E4	0.251666E5	F
24.45	40119600	0.122699E4	0.326967E5	F
24.95	37302900	0.939086E3	0.397225E5	F
25.45	31698000	0.715140E3	0.443241E5	F
25.95	23300100	0.541717E3	0.430115E5	F
26.45	13676400	0.407839E3	0.335338E5	F
26.95	6906420	0.304837E3	0.226561E5	F
27.45	3199210	0.226244E3	0.141405E5	F
27.95	3902700	0.166532E3	0.234356E5	F
28.35	223140	0.129501E3	0.172307E4	L

NO-AVG 0.102791E4

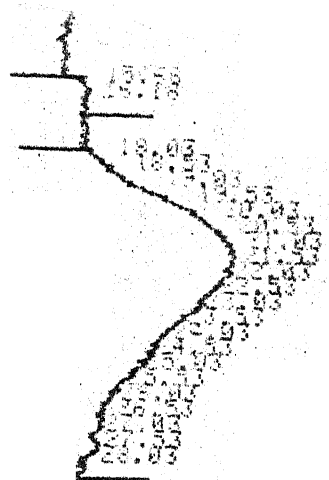
WT-AVG 0.191372E4

Z-AVG 0.304287E4

VIS-AVG 0.191307E4

DISPERSITY 0.186175E1

INTRINSIC VISCOSITY 0.191288E-2



AUG. 6/ 1982 13:51/23

CHART 0.50 CM/MIN

COLUMNS: 10<sup>4</sup>Å, 10<sup>3</sup>Å, 500Å

RUN #1

CALC. #1

SOLVENT: CHLOROFORM

SPR 10

## GPC QUANTITATION

## CHROMATOGRAM OF SAMPLE 3

RT	AREA	MOL WT	AMW	
18.03	2307530	0.338070E5	0.682559E2	F
18.53	7515030	0.258635E5	0.290565E3	F
19.03	14585200	0.198699E5	0.734034E3	F
19.53	24788700	0.153179E5	0.161828E4	F
20.03	33990400	0.118407E5	0.287064E4	F
20.53	40233300	0.917001E4	0.438749E4	F
21.03	44055300	0.711180E4	0.619467E4	F
21.53	45265300	0.552052E4	0.819946E4	F
22.03	43476800	0.428386E4	0.101489E5	F
22.53	39075000	0.332171E4	0.117635E5	F
23.03	35479400	0.257229E4	0.137929E5	F
23.53	29617400	0.198809E4	0.148974E5	F
24.03	24658900	0.153194E4	0.160965E5	F
24.53	21838100	0.117622E4	0.185663E5	F
25.03	18002400	0.899379E3	0.200164E5	F
25.53	13040400	0.684319E3	0.190560E5	F
26.03	9501830	0.517986E3	0.184982E5	F
26.53	7321160	0.389481E3	0.187972E5	F
27.03	6021800	0.290856E3	0.207037E5	F
27.53	5625250	0.215565E3	0.260953E5	F
28.03	2418760	0.158486E3	0.152616E5	F
28.43	737973	0.123017E3	0.599895E4	EL

NO-AVG 0.184855E4

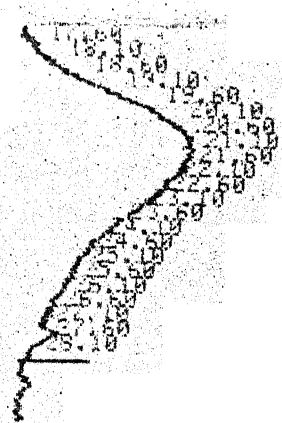
WT-AVG 0.605260E4

Z-AVG 0.111500E5

DIS-AVG 0.605079E4

DISPERSITY 0.327424E1

INTRINSIC VISCOSITY 0.605076E-2



AUG. 6. 1982 14.34.43

CHART: 0.50 CM/MIN

COLUMN: 10<sup>3</sup>A<sup>+</sup>, 10<sup>3</sup>A<sup>+</sup>, 500A<sup>+</sup>

RUN #2

SOLVENT: CHLOROFORM

CALL #1

OPR 10

5

GPC QUANTITATION

CHROMATOGRAM OF SAMPLE 3 (REPEAT)

RT	AREA	MOL WT	Q/MIN	
17.60	1203640	0.427147E5	0.281785E2	F
18.10	5100370	0.325497E5	0.156694E3	F
19.60	11682900	0.249190E5	0.468835E3	F
19.10	21465700	0.191536E5	0.112071E4	F
19.60	32877500	0.147705E5	0.222588E4	F
20.10	42159800	0.114217E5	0.369120E4	F
20.60	49184000	0.884829E4	0.555858E4	F
21.10	51758600	0.686275E4	0.754196E4	F
21.60	50590500	0.532613E4	0.949854E4	F
22.10	47785000	0.413358E4	0.115601E5	F
22.60	43337100	0.320472E4	0.135228E5	F
23.10	37737400	0.248096E4	0.152108E5	F
23.60	31247300	0.191670E4	0.163026E5	F
24.10	25894400	0.147630E4	0.175400E5	F
24.60	20909200	0.113291E4	0.184561E5	F
25.10	17132200	0.865839E3	0.197868E5	F
25.60	14934800	0.658403E3	0.226833E5	F
26.10	12064200	0.497771E3	0.242364E5	F
26.60	9206860	0.374017E3	0.246161E5	F
27.10	6759220	0.279060E3	0.242213E5	F
27.60	8320240	0.208583E3	0.402755E5	F
28.10	3460270	0.151632E3	0.228201E5	F
28.42	368997	0.123839E3	0.297965E4	L

NO-AVG 0.179039E4  
 WT-AVG 0.648747E4  
 12-AVG 0.126786E5  
 VIS-AVG 0.648598E4

DISPERSITY 0.362349E1  
 INTRINSIC VISCOSITY 0.648535E-2

GPC takes the curve to be continuous. This can be avoided only if the resolution is improved by use of other columns. As they were not available, the analysis could not be improved. The results of GPC are also presented in Table 3. Considering the difficulty with resolution, the disagreement between GPC results and others can not be commented upon.

$\bar{M}_n$  can also be calculated from analytical results.

It is given by

$$\bar{M}_n = \frac{\text{Equivalent weight of KOH} \times 10^3}{(\text{Acid number} + \text{hydroxyl number})/2}$$

These results are also presented in Table 3. The agreement between theory and experiment can be considered satisfactory.

It can be concluded that the experimental set up is to be modified to get better vacuum for making high molecular weight resins and that columns have to be added to GPC to get better resolution. Monitoring of glycol concentration in the condensate is also necessary. For the given set up the agreement between theory and experiment is satisfactory.

Table 3

COMPARISON BETWEEN THEORETICAL AND EXPERIMENTAL RESULTS

Resin number.	$\bar{M}_n$ Analytical	$\bar{M}_n$ Theory	PDI	$\bar{M}_n$ GPC	PDI
1	814	728	3.76	~350	1.7
2	1365	1316	4.40	~890	2.2
3	2513	2665	4.40	~1790	3.6

## CHAPTER 5

### CONCLUSIONS

It was shown that the MWD for reversible as well as irreversible step polymerisation with unequal reactivities are identical if it is assumed that in a given species all internal arrangements are equally probable.

An algorithm given by Vimala and Nath was used to solve the linear simultaneous partial differential equations describing simultaneous diffusion and polycondensation and the results compared well with the exact solution available.

The experimental setup designed to make polyesters has to be modified to get better vacuum for making high molecular weight resins. Some additional columns have to be added to GPC to get better resolution. Monitoring of glycol and water in the condensate may be necessary to calculate MWD.

REFERENCES

1. Case, L.C., J. Polym. Sci., 29, 455 (1958)
2. Gandhi, K.S., and Babu, S.V., A.I.Ch.E.J., 25, 266 (1979)
3. Somu, N., 'Simulation of Polyester Reactors', M.Tech.thesis, I.I.T. Kanpur (1982)
4. Hoftyzer, P.J., Vankrevelen, D.W., Proceedings of the Fourth European Symposium, Brussels, Sept.(1968)
5. Vimala, C.S., and Nath, G., J.Fluid. Mech., 10, 561 (1975)
6. Sherwood, T.K., and Pigford, R.L., "Absorption and Extraction", McGraw Hill, New York (1952).